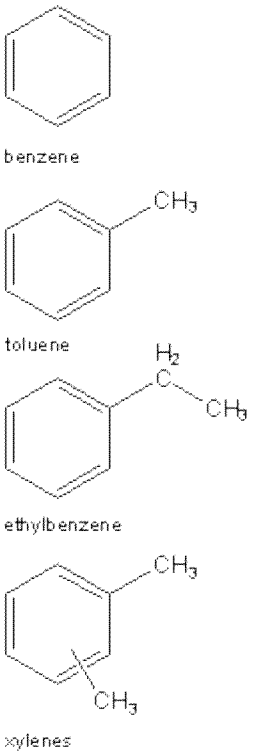
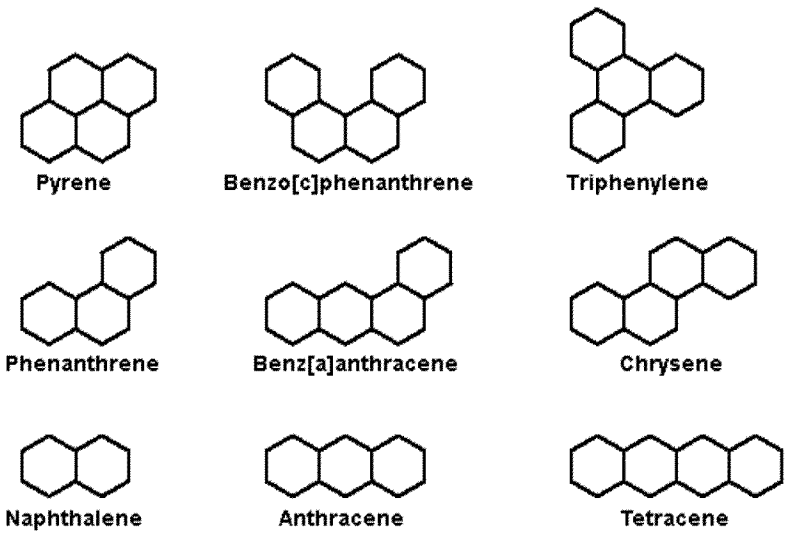
Aromatics & Gasoline: Impacts on Emissions, Air Quality, and Health

Subject matter highlights prepared by ORD and OTAQ for Administrator McCarthy





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Objectives

- Review the evidence that fuel-related aromatics posited as a primary concern in
  - primary emissions of PM and PAHs (polycyclic aromatics)
  - SOA (secondary organic aerosol) formation

  underlie both direct and indirect health outcomes.

- Provide the rationale for the tenuous level of confidence for using this knowledge-base for associated policy decisions.

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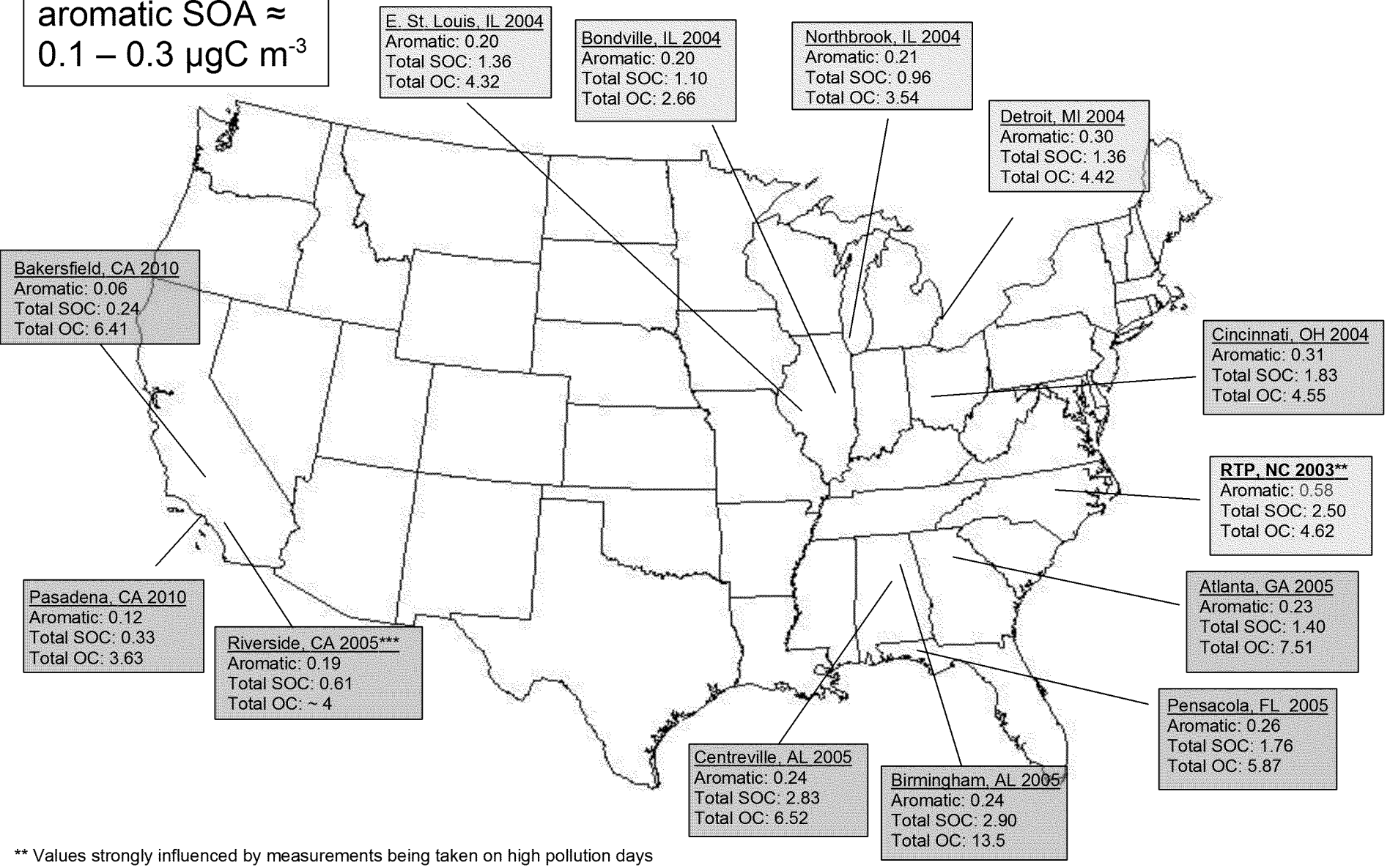
Take-Home Messages

- The contribution of fuel-based aromatics in SOA formation is real but complex; any fuel producing NO_x and O_3 contributes to SOA
- SOA and PAHs have been linked with a number of health outcomes but via uncertain mechanisms
- The epidemiological links between aromatics in fuels or its SOA products to disorders such as *autism spectrum (ASD) and attention deficit (ADD) disorders* are weak largely due to poor exposure metrics
- At this time, the science on aromatics is too uncertain to support definitive policy decisions

Ambient Concentrations of Aromatic SOA

New data confirm aromatic SOA ≈ 0.1 – 0.3 μgC m^{-3}

7 new data sets shown in orange



** Values strongly influenced by measurements being taken on high pollution days

*** Based on initial data analysis of aggregated weekend-weekday samples

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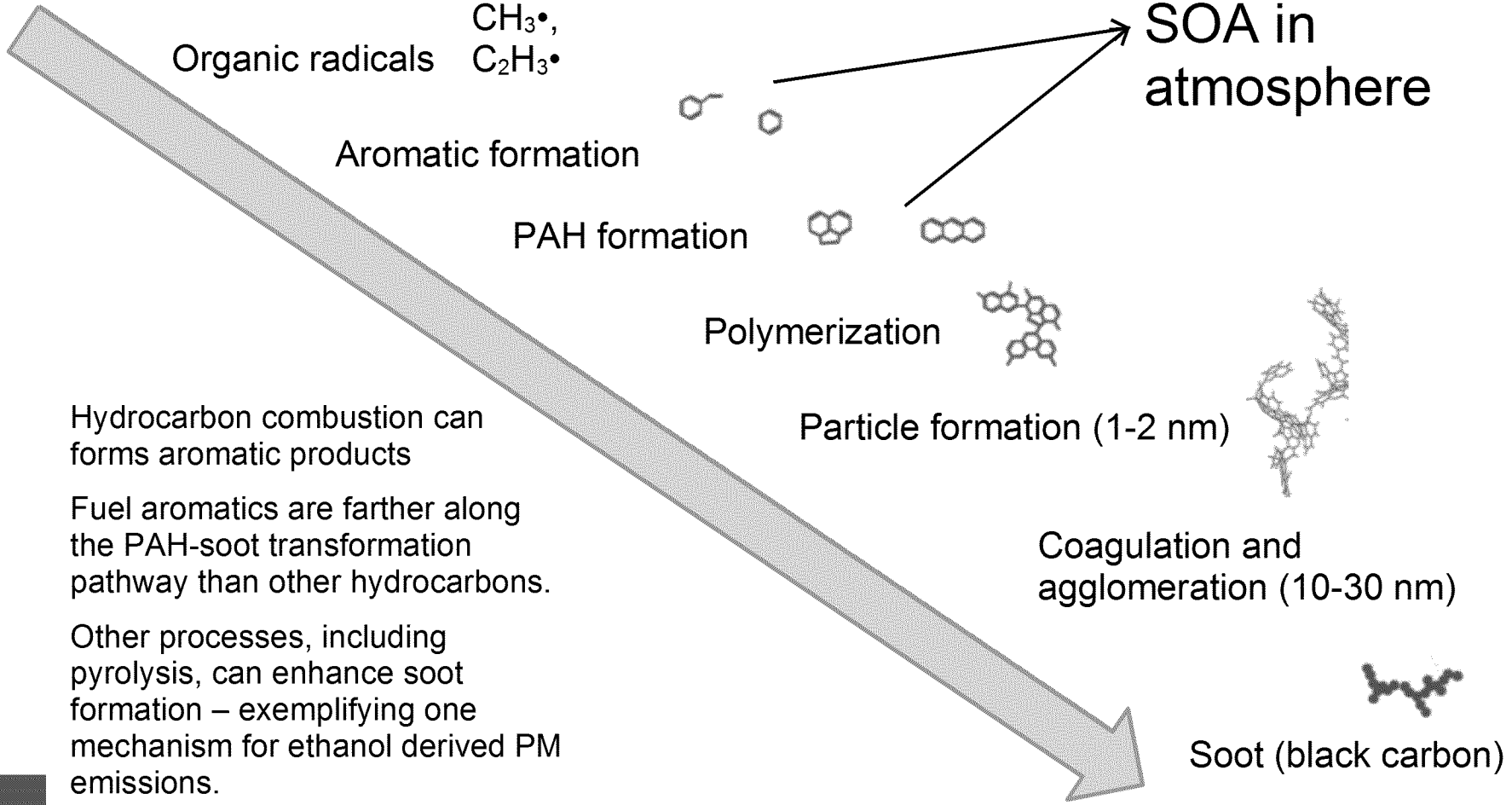
Aromatics in Emissions

- Gasoline may contain ~15-~35% aromatics by volume to increase octane
  - Other octane boosters: branched alkanes, ethanol, other oxygenates
- Fuel regulations affect aromatics content
  - RFS1 and RFS2 require blending of ethanol into gasoline
  - EPA's Mobile Source Air Toxics (MSAT) rule limits benzene, a leukemogen
  - CARB's reformulated gasoline rule limits aromatics in gasoline to 25%
- Ethanol advocates assert that replacing aromatics with ethanol in gasoline will reduce many air quality and health problems
- Gasoline engine emissions are precursors for secondary pollutants
  - Primary emissions include black carbon (soot), polycyclic aromatic hydrocarbons (PAHs), and air toxics (e.g., benzene)
  - Secondary precursors include NOx and VOCs (including aromatics like toluene)
- Gasoline fuel properties and its blended forms affect emissions
  - Aromatics content increases PM, NOx, and aromatics emissions
  - Ethanol content also increases PM and NOx emissions

Aromatics and PAHs Form During Combustion and Contribute to Soot



Hydrocarbon combustion can forms aromatic products

Fuel aromatics are farther along the PAH-soot transformation pathway than other hydrocarbons.

Other processes, including pyrolysis, can enhance soot formation – exemplifying one mechanism for ethanol derived PM emissions.

Summary of Epidemiology Studies:

PAHs and Autism Spectrum Disorders (ASD) or Attention Deficit Disorders (ADD) - BACKGROUND

- Literature search identified 5 studies that examined ASD or ADD
  - Four studies conducted in the U.S.: Windham et al. (2006)-San Francisco; Kalkbrenner et al. (2010)-North Carolina and West Virginia; Perera et al. (2012)-NYC; Roberts et al. (2013)-14 U.S. cities
  - One study conducted in Poland

- All U.S. studies, except Perera et al. (2012) which conducted a personal monitoring campaign, estimated PAH exposures using modeled annual average HAPs concentrations from EPA NATA model
  - NATA output accuracy varies by pollutant due to incompleteness of emissions inventory inputs; also not all pollutants are monitored in every location

Summary of Epidemiology Studies:

PAHs and Autism Spectrum Disorders (ASD) or Attention Deficit Disorders (ADD) - RESULTS

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– Studies using NATA exposure data

- Positive associations observed between exposure to aromatic solvents (Windham et al. 2006), as well as quinoline and styrene (Kalkbrenner et al. 2010) and ASD
- Largest U.S.-based study utilizing the Nurses' Health Study cohort found no evidence of an association between any PAHs (i.e., styrene and quinoline) and ASD (Roberts et al. 2013)

– Study using personal exposure data

- Found positive associations between high prenatal PAH exposure (measured by personal monitoring and a biomarker) and symptoms of anxious/depressed and attention problems (Perera et al. 2012)
- Important to note exposure represented an integrated indoor/outdoor exposure

Conclusions from Epidemiology Studies:

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PAHs and Autism Spectrum Disorders (ASD) or Attention Deficit Disorders (ADD) - CONCLUSIONS

- Studies report some evidence of an association between PAH exposure and neurobehavioral disorders
- Uncertainties remain in these studies specifically with respect to the validity of using NATA data to estimate exposure to PAHs
- Other studies have shown associations between PAHs and various health endpoints (e.g, cancer)
- Even though associations with PAHs observed in the studies highlighted it is important to note the results of these studies are consistent with the conclusions of the 2009 PM ISA:
  - *"… many constituents of PM can be linked with differing health effects and the evidence is not yet sufficient to allow differentiation of those constituents or sources that are more closely related to specific health outcomes (Section 2.4.4)."*

Health Effects of Aromatic SOA

- The PM ISA considered the potential health effects of the many chemical components and sources of $PM_{2.5}$ (PM ISA, 2009; Stanek et al., 2009).
- No studies specifically investigated the health effects of aromatic SOA, though several looked at the total organic fraction of $PM_{2.5}$.

Stanek LW et al. Attributing health effects to apportioned components and sources of particulate matter: An evaluation of collective results. Atmos Eviron; 45: 5655-63.

Multiple chemical components and sources of $PM_{2.5}$ have been linked to various health effects (i.e., respiratory, cardiovascular, and mortality), but there is no consistent pattern of causation

Inhalation Effects of Aromatics vs. Ethanol

- Acute exposure
  - Potency: aromatics > ethanol by factor of 400
  - Ethanol poorly absorbed by inhalation
  - Same neurological targets and effects
  - Effects depend on concentration in brain at time of measurement

- Developmental exposure
  - Substantial database for ingested ethanol, few data on inhaled aromatics or ethanol
  - Occupational aromatics: Mixed evidence for effects on behavior and physiology

- Repeated exposure
  - Abuse (high exposures) of aromatics can lead to CNS myelinopathy, cognitive and motor deficits
  - Occupational exposures to aromatics can produce sensory, cognitive, immune dysfunction and cancer (benzene)

- Inhaled ethanol produces much lower internal doses than inhaled aromatics.
- Health endpoints of inhaled ethanol and aromatics are similar, but less is known about inhaled ethanol.

Health Effects of Aromatic SOA

- Recent toxicological study has begun to examine whether there are differences in health effects due to fresh versus aged emissions.:
  - McDonald JD et al. Cardiopulmonary response to inhalation of biogenic secondary organic aerosol. Inhal Toxicol. 2010 Feb; 22(3):253-65.
  - Zielinska B et al. Atmospheric transformation of diesel emissions. Res Rep Health Eff Inst. 2010 Apr; (147): 5-60.
  - Papapostolou V et al. Laboratory evaluation of a prototype photochemical chamber designed to investigate the health effects of fresh and aged vehicular exhaust emissions. Inhal Toxicol. 2011 Jul; 23(8): 495-505.
  - Rager JE et al. A toxicogenomic comparison of primary and photochemically altered air pollutant mixtures. Environ Health Perspect. 2011 Nov; 119(11): 1583-9.

No consistent pattern has emerged, but ORD continues to sponsor this research and monitor the relevant literature.

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Vehicle and Near Road Studies

- ORD has been measuring motor vehicle emissions of speciated PM (including PAHs) and VOCs (including BTEX)
  - Light-duty and heavy-duty vehicles
  - Different fuels types (including alternative fuels such as ethanol gasoline and biodiesel)
  - Varied operating conditions.
- ORD also has collected speciated PM and VOC data at varying distances from major highways in the US as part of a comprehensive near road emissions-exposure-health studies.

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Aromatics in AQ Modeling

- ORD scientists developed the first (and, to-date, only) method for quantifying the amount of ambient $PM_{2.5}$ that originates from aromatics.
- These unique ambient data were used to develop a state-of-the-art formula for predicting aromatic $PM_{2.5}$ levels that is now embedded in the EPA's Community Multiscale Air Quality (CMAQ) model.
- CMAQ predicts: **If aromatics were *entirely* removed from gasoline, the amount of ambient $PM_{2.5}$ inhaled by the U.S. population would decrease by only 1.4%.**

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Related Ongoing Aromatics Research

- Emissions of aromatics from co-firing blends of biomass and coal
- Fugitive and area source emissions of aromatics around natural gas wells – R6
- Application of passive monitors to evaluate local impacts – R3, R5, R6 and R8
- Health effects and atmospheric chemistry of multipollutant atmospheres including aromatics
- Chemical speciation of PM (PAHs, nitro-PAHs) in ambient air and source emissions

Some Reflections: EFC/NIEHS PM and Vehicle Emissions Mtg

- The audience was overwhelmingly biofuels / ethanol industry reps
  - Interestingly: Apparent lack of petro and motor vehicle industry representation yet they were supposedly invited; few scientists other than the panels; a couple press
  - C. Boyden Gray opened with an intro on his perceptions of the pressing concerns of near road exposures due to motor fuel burning and the formation of ultrafine particles (UFPs) and polycyclic aromatic compounds (PAHs) – and a role for clean fuels.
- The panel discussions were well conducted and transparent
  - The science generally current but not comprehensive
  - Nothing really "new" revealed in the panels – mostly scoping the problem
  - Health implications are suggested but the exposure foundation is porous
  - A couple self-serving questions from EFC: *Shouldn't we be burning cleaner fuels? Wouldn't you want to reduce PAHs by 50%?*
- No substantive policy agenda was pushed but the mtg concluded with the announcement of a follow-up policy mtg (tent. May 20)
  - Sponsors intend to get all appropriate parties together for this policy meeting
  - Rationale: "the day's proceedings confirm the need for immediate action at the policy level – a bit of a leap perhaps given the nature of the discussions

Conclusions

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- SOA formation constitutes highly complex chemical processes
- The contribution of aromatics from fuels in SOA formation appears to be finite but minor – but much uncertainty remains
- Any fuel producing NOx and O3 also contribute to SOA
- SOA and PAHs have been linked with a number of health outcomes but via uncertain mechanisms
- Persistent adverse neurological health outcomes from chronic exposure to aromatic compounds are found at high occupational exposures that are often weak in exposure metrics
- Changes in any one fuel property (e.g., aromatics) may or may not reduce ambient SOA – *comprehensive strategies are needed*
- At this time, the science on aromatics is too uncertain to support definitive policy decisions